

## HIGH-VOLUME AIR SAMPLER CALIBRATION WORKSHEET

Site Location: \_\_\_\_\_  
 Date: \_\_\_\_\_ Barometric Pressure,  $P_2$  mm Hg (or kPa) \_\_\_\_\_  
 Calibrated By: \_\_\_\_\_ Temperature,  $T_2$  (K) \_\_\_\_\_  
 Sampler No. \_\_\_\_\_ Serial No. \_\_\_\_\_  
 Transfer std. type: \_\_\_\_\_ Serial No. \_\_\_\_\_

$P_{std} = 760 \text{ mm Hg (or 101 kPa)}$ Optional: Average barometric pressure: $P_a =$ _____ Seasonal average temperature: $T_a =$ _____				(Y)	
No.	Pressure drop across orifice (in or mm) of water	$Q_{std}$ (from orifice certification) std m <sup>3</sup> /min	Sampler flow rate indication (arbitrary)	For specific pressure and temperature corrections (see Table 1): <input type="checkbox"/> 1 <input type="checkbox"/> $\sqrt{\frac{P_2}{P_a} \frac{T_a}{T_2}}$ or <input type="checkbox"/> $\sqrt{\frac{P_2}{P_{std}} \frac{T_a}{T_2}}$	For incorporation of average pressure and seasonal average temperature (see Table 1): <input type="checkbox"/> 1 <input type="checkbox"/> $\sqrt{\frac{P_2}{P_a} \frac{T_a}{T_2}}$ or <input type="checkbox"/> $\sqrt{\frac{P_2}{P_{std}} \frac{T_a}{T_2}}$
1					
2					
3					
4					
5					
6					

## LEAST SQUARES CALCULATIONS

Linear regression of Y on X:  $Y = mX + b$ ; Y = appropriate expression from Table 1; X =  $Q_{std}$ .

Slope (m) = \_\_\_\_\_ Intercept (b) = \_\_\_\_\_ Correlation Coeff. (r) = \_\_\_\_\_

To determine subsequent flow rate during use:  $X = \frac{1}{m} (Y - b)$ ;

$Q_{std} = \frac{1}{m} ([\text{appropriate expression from Table 2}] - b)$

Figure 5. Example of high-volume air sampler calibration worksheet.

[47 FR 54912, Dec. 6, 1982; 48 FR 17355, Apr. 22, 1983]

# APPENDIX C TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF CARBON MONOXIDE IN THE ATMOSPHERE (NON-DISPERSIVE INFRARED PHOTOMETRY)

## 1.0 APPLICABILITY

1.1 This non-dispersive infrared photometry (NDIR) Federal Reference Method (FRM) provides measurements of the concentration of carbon monoxide (CO) in ambi-

ent air for determining compliance with the primary and secondary National Ambient Air Quality Standards (NAAQS) for CO as specified in §50.8 of this chapter. The method is applicable to continuous sampling and measurement of ambient CO concentrations suitable for determining 1-hour or longer average measurements. The method may also provide measurements of shorter averaging times, subject to specific analyzer performance limitations. Additional CO monitoring quality assurance procedures and guidance

are provided in part 58, appendix A, of this chapter and in reference 1 of this appendix C.

## 2.0 MEASUREMENT PRINCIPLE

2.1 Measurements of CO in ambient air are based on automated measurement of the absorption of infrared radiation by CO in an ambient air sample drawn into an analyzer employing non-wavelength-dispersive, infrared photometry (NDIR method). Infrared energy from a source in the photometer is passed through a cell containing the air sample to be analyzed, and the quantitative absorption of energy by CO in the sample cell is measured by a suitable detector. The photometer is sensitized specifically to CO by employing CO gas in a filter cell in the optical path, which, when compared to a differential optical path without a CO filter cell, limits the measured absorption to one or more of the characteristic wavelengths at which CO strongly absorbs. However, to meet measurement performance requirements, various optical filters, reference cells, rotating gas filter cells, dual-beam configurations, moisture traps, or other means may also be used to further enhance sensitivity and stability of the photometer and to minimize potential measurement interference from water vapor, carbon dioxide (CO<sub>2</sub>), or other species. Also, various schemes may be used to provide a suitable zero reference for the photometer, and optional automatic compensation may be provided for the actual pressure and temperature of the air sample in the measurement cell. The measured infrared absorption, converted to a digital reading or an electrical output signal, indicates the measured CO concentration.

2.2 The measurement system is calibrated by referencing the analyzer's CO measurements to CO concentration standards traceable to a National Institute of Standards and Technology (NIST) primary standard for CO, as described in the associated calibration procedure specified in section 4 of this reference method.

2.3 An analyzer implementing this measurement principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter.

2.4 *Sampling considerations.* The use of a particle filter in the sample inlet line of a CO FRM analyzer is optional and left to the discretion of the user unless such a filter is specified or recommended by the analyzer manufacturer in the analyzer's associated operation or instruction manual.

## 3.0 INTERFERENCES

3.1 The NDIR measurement principle is potentially susceptible to interference from water vapor and CO<sub>2</sub>, which have some infrared absorption at wavelengths in common with CO and normally exist in the atmos-

phere. Various instrumental techniques can be used to effectively minimize these interferences.

## 4.0 CALIBRATION PROCEDURES

4.1 *Principle.* Either of two methods may be selected for dynamic multipoint calibration of FRM CO analyzers, using test gases of accurately known CO concentrations obtained from one or more compressed gas cylinders certified as CO transfer standards:

4.1.1 *Dilution method:* A single certified standard cylinder of CO is quantitatively diluted as necessary with zero air to obtain the various calibration concentration standards needed.

4.1.2 *Multiple-cylinder method:* Multiple, individually certified standard cylinders of CO are used for each of the various calibration concentration standards needed.

4.1.3 Additional information on calibration may be found in Section 12 of reference 1.

4.2 *Apparatus.* The major components and typical configurations of the calibration systems for the two calibration methods are shown in Figures 1 and 2. Either system may be made up using common laboratory components, or it may be a commercially manufactured system. In either case, the principal components are as follows:

4.2.1 CO standard gas flow control and measurement devices (or a combined device) capable of regulating and maintaining the standard gas flow rate constant to within  $\pm 2$  percent and measuring the gas flow rate accurate to within  $\pm 2$  percent, properly calibrated to a NIST-traceable standard.

4.2.2 For the dilution method (Figure 1), dilution air flow control and measurement devices (or a combined device) capable of regulating and maintaining the air flow rate constant to within  $\pm 2$  percent and measuring the air flow rate accurate to within  $\pm 2$  percent, properly calibrated to a NIST-traceable standard.

4.2.3 Standard gas pressure regulator(s) for the standard CO cylinder(s), suitable for use with a high-pressure CO gas cylinder and having a non-reactive diaphragm and internal parts and a suitable delivery pressure.

4.2.4 Mixing chamber for the dilution method of an inert material and of proper design to provide thorough mixing of CO standard gas and diluent air streams.

4.2.5 Output sampling manifold, constructed of an inert material and of sufficient diameter to ensure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure nearly atmospheric pressure at the analyzer connection port and to prevent ambient air from entering the manifold.

## 4.3 Reagents

4.3.1 CO gas concentration transfer standard(s) of CO in air, containing an appropriate

concentration of CO suitable for the selected operating range of the analyzer under calibration and traceable to a NIST standard reference material (SRM). If the CO analyzer has significant sensitivity to CO<sub>2</sub>, the CO standard(s) should also contain 350 to 400 ppm CO<sub>2</sub> to replicate the typical CO<sub>2</sub> concentration in ambient air. However, if the zero air dilution ratio used for the dilution method is not less than 100:1 and the zero air contains ambient levels of CO<sub>2</sub>, then the CO standard may be contained in nitrogen and need not contain CO<sub>2</sub>.

4.3.2 For the dilution method, clean zero air, free of contaminants that could cause a detectable response on or a change in sensitivity of the CO analyzer. The zero air should contain <0.1 ppm CO.

#### 4.4 Procedure Using the Dilution Method

4.4.1 Assemble or obtain a suitable dynamic dilution calibration system such as

the one shown schematically in Figure 1. Generally, all calibration gases including zero air must be introduced into the sample inlet of the analyzer. However, if the analyzer has special, approved zero and span inlets and automatic valves to specifically allow introduction of calibration standards at near atmospheric pressure, such inlets may be used for calibration in lieu of the sample inlet. For specific operating instructions, refer to the manufacturer's manual.

4.4.2 Ensure that there are no leaks in the calibration system and that all flowmeters are properly and accurately calibrated, under the conditions of use, if appropriate, against a reliable volume or flow rate standard such as a soap-bubble meter or wet-test meter traceable to a NIST standard. All volumetric flow rates should be corrected to the same temperature and pressure such as 298.15 K (25 °C) and 760 mm Hg (101 kPa), using a correction formula such as the following:

$$F_c = F_m \frac{298.15 \times P_m}{760(T_m + 273.15)} \quad (1)$$

Where:

$F_c$  = corrected flow rate (L/min at 25 °C and 760 mm Hg),

$F_m$  = measured flow rate (at temperature  $T_m$  and pressure  $P_m$ ),

$P_m$  = measured pressure in mm Hg (absolute), and

$T_m$  = measured temperature in degrees Celsius.

4.4.3 Select the operating range of the CO analyzer to be calibrated. Connect the measurement signal output of the analyzer to an appropriate readout instrument to allow the analyzer's measurement output to be continuously monitored during the calibration. Where possible, this readout instrument should be the same one used to record routine monitoring data, or, at least, an instrument that is as closely representative of that system as feasible.

4.4.4 Connect the inlet of the CO analyzer to the output-sampling manifold of the calibration system.

4.4.5 Adjust the calibration system to deliver zero air to the output manifold. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to ensure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until a stable response is obtained. After the response has stabilized, adjust the analyzer zero reading.

4.4.6 Adjust the zero air flow rate and the CO gas flow rate from the standard CO cylinder to provide a diluted CO concentration of approximately 80 percent of the measurement upper range limit (URL) of the operating range of the analyzer. The total air flow rate must exceed the total demand of the analyzer(s) connected to the output manifold to ensure that no ambient air is pulled into the manifold vent. The exact CO concentration is calculated from:

$$[CO]_{OUT} = \frac{[CO]_{STD} \times F_{CO}}{F_D + F_{CO}} \quad (2)$$

Where:

$[CO]_{OUT}$  = diluted CO concentration at the output manifold (ppm),

$[CO]_{STD}$  = concentration of the undiluted CO standard (ppm),

$F_{CO}$  = flow rate of the CO standard (L/min),  
and

$F_D$  = flow rate of the dilution air (L/min).

Sample this CO concentration until a stable response is obtained. Adjust the analyzer span control to obtain the desired analyzer response reading equivalent to the calculated standard concentration. If substantial adjustment of the analyzer span control is required, it may be necessary to recheck the zero and span adjustments by repeating steps 4.4.5 and 4.4.6. Record the CO concentration and the analyzer's final response.

4.4.7 Generate several additional concentrations (at least three evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing  $F_{CO}$  or increasing  $F_D$ . Be sure the total flow exceeds the analyzer's total flow demand. For each concentration generated, calculate the exact CO concentration using equation (2). Record the concentration and the analyzer's stable response for each concentration. Plot the analyzer responses (vertical or y-axis) versus the corresponding CO concentrations (horizontal or x-axis). Calculate the linear regression slope and intercept of the calibration curve and verify that no point deviates from this line by more than 2 percent of the highest concentration tested.

4.5 Procedure Using the Multiple-Cylinder Method. Use the procedure for the dilution method with the following changes:

4.5.1 Use a multi-cylinder, dynamic calibration system such as the typical one shown in Figure 2.

4.5.2 The flowmeter need not be accurately calibrated, provided the flow in the output manifold can be verified to exceed the analyzer's flow demand.

4.5.3 The various CO calibration concentrations required in Steps 4.4.5, 4.4.6, and 4.4.7 are obtained without dilution by selecting zero air or the appropriate certified standard cylinder.

4.6 Frequency of Calibration. The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checking, will vary by analyzer. However, the minimum frequency, acceptance criteria, and subsequent actions are specified in reference 1, appendix D, "Measurement Quality Objectives and Validation Template for CO" (page 5 of 30). The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of CO analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, routine maintenance, and quality control.

#### 5.0 REFERENCE

1. *QA Handbook for Air Pollution Measurement Systems—Volume II. Ambient Air Quality Monitoring Program*. U.S. EPA. EPA-454/B-08-003 (2008).

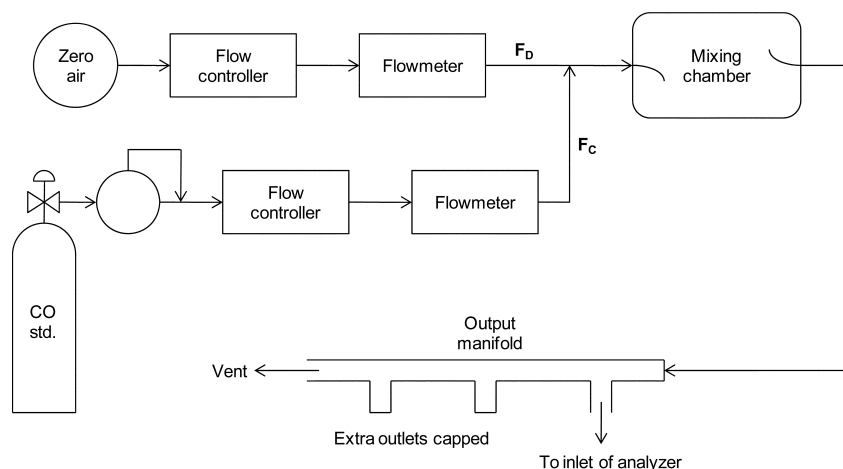


Figure 1. Dilution method for calibration of CO analyzers.

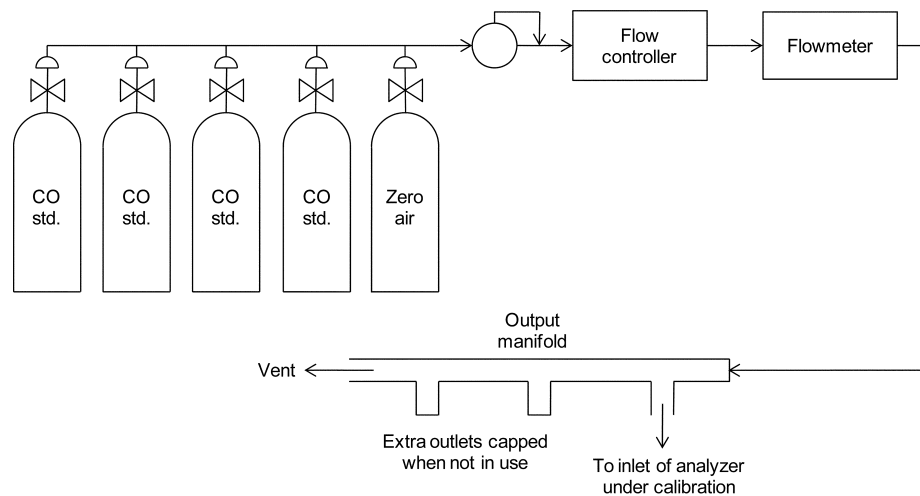


Figure 2. Multiple cylinder method for calibration of CO analyzers.

[76 FR 54323, Aug. 31, 2011]

#### APPENDIX D TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF OZONE IN THE ATMOSPHERE

##### MEASUREMENT PRINCIPLE

1. Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light, which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

2. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter and calibrated as follows:

##### CALIBRATION PROCEDURE

1. *Principle.* The calibration procedure is based on the photometric assay of ozone ( $O_3$ ) concentrations in a dynamic flow system. The concentration of  $O_3$  in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of (1) the absorption coefficient ( $\alpha$ ) of  $O_3$  at 254 nm, (2) the optical path length ( $l$ ) through the sample, (3) the transmittance of the sample at a wavelength of 254 nm, and (4) the temperature ( $T$ ) and pressure ( $P$ ) of the sample. The transmittance is defined as the ratio  $I/I_0$ , where  $I$  is the intensity of light which passes through the cell and is sensed

by the detector when the cell contains an  $O_3$  sample, and  $I_0$  is the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of  $I$  and  $I_0$ . The quantities defined above are related by the Beer-Lambert absorption law,

$$\text{Transmittance} = \frac{I}{I_0} = e^{-\alpha cl} \quad (1)$$

where:

$\alpha$  = absorption coefficient of  $O_3$  at 254 nm =  $308 \pm 4 \text{ atm}^{-1} \text{ cm}^{-1}$  at  $0^\circ \text{C}$  and 760 torr. <sup>3(1 2 3 4 5 6 7)</sup>

$c$  =  $O_3$  concentration in atmospheres

$l$  = optical path length in cm

In practice, a stable  $O_3$  generator is used to produce  $O_3$  concentrations over the required range. Each  $O_3$  concentration is determined from the measurement of the transmittance ( $I/I_0$ ) of the sample at 254 nm with a photometer of path length  $l$  and calculated from the equation,

$$c(\text{atm}) = -\frac{1}{\alpha l} (\ln I / I_0) \quad (2a)$$

or

$$c(\text{ppm}) = -\frac{10^6}{\alpha l} (\ln I / I_0) \quad (2b)$$